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March 30, 1854.

THOMAS BELL, Esq., V.P., in the Chair.

The following papers were read :—

- I. "Note on the Melting-point and Transformations of Sulphur." By B. C. BRODIE, Esq., F.R.S. Received March 30, 1854.

In the treatises of chemistry where the results of different observers are collected, various statements will be found as to the melting-point of sulphur. The numbers given in Gmelin's Chemistry vary from $104^{\circ}\cdot5$ C. to $112^{\circ}\cdot2$ C., but of five chemists cited, no two agree as to this apparently simple fact. There is evidently some peculiarity about this melting-point which is the cause of these anomalous results. In some experiments on allotropic substances, in which I have been engaged, I had occasion to submit this question to a more searching inquiry than it had hitherto received, in which I have discovered the cause of these discrepancies. In the present note I will briefly give the results at which I have arrived, reserving the details for a further and more full communication.

The melting-point of sulphur varies according to its allotropic condition. This condition is readily altered by heat, and invariably, without peculiar precautions, by melting. Hence the temperature at which sulphur melts is different from that at which it will solidify, or at which, having been melted, it will melt again.

The melting-point of the octohedral sulphur, as crystallized from the bisulphide of carbon, is $114^{\circ}\cdot5$ C. But from the facility with which this sulphur, when heated even below its melting-point, passes into the sulphur of the oblique system, this fact may readily be overlooked. When this sulphur, in the state of fine powder, is heated even for the shortest time between 100° and $114^{\circ}\cdot5$, this change cannot be avoided. For the transformation of large crystals

a longer time is required. At a certain point the crystal becomes opaque, and is often broken in pieces at the moment of the change. When in such a crystal this change has either entirely or partially taken place, the melting-point will be above $114^{\circ}5$. The minute crystals of sulphur from alcohol, which are so extremely thin that their angles cannot be measured, have this melting-point of $114^{\circ}5$, which fixes the system to which the crystals belong. The crystals of sulphur from benzole (rectified coal naphtha) melt also at $114^{\circ}5$. The crystals from alcohol are very minute, consequently so readily transformed, that they presented anomalies which led me to doubt whether sulphur of both forms did not exist among them. I answered this question by dividing a certain number of carefully selected crystals, and taking the melting-point of the two halves of the same crystal. I found that these melting-points in many cases did not correspond, which would have been the case if the anomalies had arisen from the different nature of the crystals. Sulphur which has been melted at $114^{\circ}5$, and of which the temperature has not been raised above 115° , remains, on solidification, perfectly transparent for any length of time. Heated beyond this point, it becomes, on cooling, more or less opaque.

When sulphur has been converted by heating for a sufficient length of time, in the manner above mentioned, between 100° and $114^{\circ}5$, it acquires a fixed melting-point of 120° C. This is the melting-point of the oblique prismatic sulphur. If sulphur thus converted be carefully melted so as to raise the temperature as little as possible above the melting-point, no sensible difference will be observed between the point of melting and of solidification. To obtain this fixed melting-point of 120° , care must be taken that the transformation of the sulphur has been thoroughly effected. If this be not done, it may melt at any point between $114^{\circ}5$ and 120° . If, however, the temperature of the melted sulphur be raised above its melting-point of 120° , the point of solidification will be altered, and may lie even below the first melting-point of $114^{\circ}5$ *. The point of solidification is in this case not fixed, but depends upon the temperature to which the sul-

* This has been observed by Person, who states that if sulphur be heated above 150° its melting-point is lowered to about 112° or 110° . He says, that when heated with care, the thermometer will remain constant during crystallization, at 115° . I have not found this correct.—*Ann. de Chemie*, vol. xxi. p. 323.

phur is raised and upon the mode in which it is cooled. It has varied in my experiments from 118° to as low as 111° . When the melting-point of the sulphur, thus solidified, is taken, it will begin to melt at about the temperature of solidification. The cause of this anomaly is evident. When the temperature of sulphur is raised above 120° , a transformation into the viscid form instantly commences, so that the sulphur is a mixture of the two varieties, and the melting-point varies according to the proportion in which these two varieties are mixed. It varies inversely with the temperature to which the sulphur is raised, so that the presence of the viscid sulphur lowers the point of solidification. There is, however, a limit beyond which the melting-point is not affected by this admixture. I made the experiment of pouring sulphur, heated to its boiling-point, into water of different temperatures, and of taking the melting-point of the sulphur when it had become hard. Five different preparations, which, when extracted with bisulphide of carbon, gave each a different quantity of insoluble sulphur, coincided in the melting-point of about 112° . This sulphur, before melting, becomes transparent, and passes again into the viscid or elastic condition.

The sulphur which is insoluble in bisulphide of carbon, and which is prepared by extracting the hardened viscid sulphur with that reagent, has a melting-point considerably above 120° , but which I have not been able to determine with precision.

I had placed in a water-bath, at 100° , tubes containing fragments of the three definite varieties of sulphur. After a short time, on examining the tubes, I found the insoluble sulphur, which I have stated to have such a high melting-point, distinctly melted. The octohedral sulphur had become opaque and rounded at the edges, the other was unaltered in appearance. Further inquiry convinced me that the cause of the melting of the insoluble sulphur was, that it had passed into another modification, and that this conversion was attended with evolution of heat sufficient to melt the sulphur. The insoluble sulphur thus converted remains transparent, and is perfectly soluble in bisulphide of carbon.

It is stated in chemical treatises that the opacity which on solidification comes over the melted sulphur, is due to the transformation of the oblique prismatic into the octohedral sulphur, and the consequent disruption of the crystal. To this cause also is attributed the

evolution of heat which has been observed in solid sulphur immediately after cooling. There are, however, no sufficient grounds for this view, and some of the observations which I have given are decidedly adverse to it. 1. The change readily takes place, even at temperatures at which sulphur becomes opaque, in the opposite direction, namely, from the octohedron to the oblique prism. 2. The melting-point of the opaque sulphur coincides too nearly with its point of solidification for it to be supposed that this change in it has taken place. On extracting melted sulphur which had become opaque, with bisulphide of carbon, I have constantly found present traces of insoluble matter, even where the greatest precaution had been taken to avoid elevation of temperature; and this opacity appears to me to be due to the hardening of the viscid sulphur, and the consequent deposition of opaque matter in the pores of the crystals, which is quite sufficient to account for it. It remains to ascertain the cause of the evolution of the heat. On this point also I will offer a suggestion. It is well known that the appearance of opacity is delayed by pouring the sulphur into cold water, and that the sulphur thus formed is at first viscid and transparent, and only after a time becomes solid and opaque. The received view, I believe, is that the hard sulphur thus formed is the solid form of the viscid sulphur, in the same sense as ice is the solid form of water. It appears to me more probable that these two sulphurs stand in a different relation, and that the change which takes place on solidification is an allotropic transformation of the viscid sulphur into the insoluble sulphur and one of the other modifications. In the case of sulphur gradually cooled this change takes place with rapidity, and, like other similar transformations, is attended with a sensible evolution of heat. Where the sulphur is *tempered* the change takes place very slowly, and the heat evolved is not perceived. This view is confirmed by a fact which I have discovered, namely, that the viscid sulphur possesses another solid form. I have found that when sulphur, melted at a high temperature, is suddenly exposed to intense cold—the cold of solid carbonic acid and ether—the sulphur formed is not viscid, but solid, hard, and perfectly transparent. When the temperature is allowed to rise to that of the air, the sulphur becomes soft and elastic. It is probable that this is the true solid form of the viscid sulphur.